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THE INFLUENCE OF THE OXYGEN REGIME IN THE WATER COLUMN ON THE TOXICITY OF HAMILTON HARBOUR SEDIMENT

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Foreword

In its 1985 report to the International Joint Commission (IJC), the Great Lakes Water Quality Board recommended that the appropriate jurisdictions prepare and submit detailed Remedial Action Plans (RAPs) for the restoration of beneficial uses of 42 (now 43) identified "Areas of Concern" on the Great Lakes system. Hamilton Harbour is one of the 17 Canadian "Areas of Concern".

The RAP team in its 1989 Stage I report identified zones of highly contaminated sediment and presented results of a number of toxicity tests on Hamilton Harbour sediment. The cause of the toxicity was not readily attributed to any specific class of compounds. Hamilton Harbour sediment is a complex mixture of metals and trace organic compounds. As well, anaerobic conditions are periodically generated in the hypolimnion during the summer months. In order to develop options for sediment remediation, further knowledge of the causal links between sediment conditions and toxicity was required.

This report presents the results of chronic sublethal toxicity tests conducted on sediment exposed to different oxygen regimes and collected at different times during the ice-free period. This information has been presented to the Hamilton Harbour RAP team. Their comments have been incorporated into the report.

This report is intended to serve as a background reference document. It provides useful information that could assist the RAP team and the public in evaluating options and in ultimately defining a remedial action plan for the harbour. The findings and conclusions are of the author and do not necessarily represent the view or policies of the supporting agencies.

Acknowledgements

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EXECUTIVE SUMMARY

Sediment from regions within Hamilton Harbour is highly contaminated with metals, nevertheless, not all metal contaminated sites were toxic to test organisms. Most sediment did elicit sublethal and/or lethal responses in bioassay organisms. Metal bioavailability, as measured by weak acid extractions, metal bioaccumulation by fathead minnows and sediment toxicity was greater in sediment collected in the fall as compared to sediment collected in the spring. Results of analyses of tissue residues in test organisms and the reduced toxicity observed in sediment collected from some stations in the spring as compared to the fall, implicate trace metals and sediment oxygen demand as contributing to sediment toxicity. The suitability for colonization by benthic invertebrates of sediment in some areas of Hamilton Harbour appears to be limited by both contaminants and high sediment oxygen demand. Remedial options aimed at improving the oxygen regime of the harbour should result in improvements in the benthic invertebrate community directly, by providing a suitable oxygen regime for organisms less tolerant of temporal anoxia, and indirectly by decreasing metal bioavailability, possibly through the coprecipitation of trace metals with iron and manganese hydroxides.

Introduction

Trace metals and organic compounds in a substantial area of the sediment of Hamilton Harbour exceed the Ontario Ministry of Environment (MOE) sediment quality guidelines which identify the "severe effects level" (Persaud et al 1992). These are the levels at which significant biological impacts are anticipated. These concentrations in bulk sediment for Cr, Cu, Pb and Zn are 111, 114, 250 and 800 μg/g, respectively. Concentrations of these metals in the harbour sediment reach a maximum of approximately 700 (TOC 5%), 500, 160, 700 and 4500 μg/g for PAH, Cr, Cu, Pb, and Zn, respectively (Hamilton Harbour RAP Writing Team 1989).

Bulk chemical extractions of metals from sediment using hot, concentrated acids such as the *aqua regia* protocol currently in routine use the MOE laboratory, have been shown to be limited in their use for predicting site-specific environmental effects on organisms. This is due in large part to the biotic and abiotic factors that influence metal bioavailability and, consequently, metal toxicity. Numerous studies have demonstrated that the geochemistry and the physicochemical environment are important in metal speciation and subsequent bioavailability (Luoma 1983, Campbell and Tessier 1989, Davis-Colley et al 1985, Campbell et al 1987, Krantzberg and Stokes 1988). This has led to recommendations that biological tests be performed when chemical measurements indicate the potential for adverse environmental impact (Chapman 1989, Landner 1988, International Joint Commission 1988, van Veen and Stortelder 1988, Krantzberg and Bailey 1983, Karr 1987, Persaud et al 1992, Burton 1991).

Lethal and sublethal effects of chronic exposure to Hamilton Harbour sediment were expressed by nymphs of the mayfly Hexagenia limbata, the fathead minnow Pimephales promelas (Krantzberg and Boyd 1992), the oligochaete Tubifex tubifex (T. Reynoldson, pers. comm.) and acute toxicity has been reported for Pontoporia, Chironomus (Hamilton Harbour RAP Writing Team 1989), and Daphnia and

Photobacterium (Murphy, unpubl. data). From this one would anticipate significant environmental damage in nature, and a necessity to develop remedial options aimed at removing the toxicological threat.

Due to the large volume of contaminated sediment in the harbour, it may be prohibitively costly and technologically impractical to recommend immediate dredging and disposal or destruction of all sediment that exceed the provincial guidelines that identify the "severe effects level" (SEL). Painter (1992) has estimated that over 18, 12, 12 and 19 km^2 of the harbour sediment contains Cr, Cu, Pb, and Zn in excess of the SEL. This represents from 52 to 84% of the total surface area of sediment in the harbour, including Cootes Paradise. Prior to recommending full scale sediment removal or *in situ* treatment for materials that exceed the SEL, it would be extremely useful to be able to determine the extent to which metals in sediment are biologically available and are having repercussions for the health on the biota. Biological testing is also called for in the application of the provincial sediment quality guidelines.

One of the most apparent causes for the restricted benthic community observed in the harbour is the anoxia which develops in the hypolimnion during the summer months (Hamilton Harbour RAP Writing Team 1991). Alleviating the anoxia would enhance the suitability of the harbour environment for colonization by benthic organisms that are less tolerant to hypereutrophic and eutrophic conditions. The question which arises concerns the interaction between the presence of oxygen, its indirect effects of sediment toxicity particularly by altering contaminant speciation, and the ability of a richer and more abundant benthic community to bioaccumulate and mobilize contaminants from sediment into the food web.

In a previous study, the causes of sediment toxicity were investigated by selectively treating sediment with compounds designed to immobilize polar compounds, and comparing the results of bioassays using treated and untreated sediment (Krantzberg and Boyd 1992). The sediment treatments were effective in reducing toxicity in some

instances. The substances used to treat the sediment are known to chelate metals, and this assisted in demonstrating that metals contributed to the toxicity observed in chronic sediment bioassays. There was, however, evidence that sediment oxygen demand also resulted in mortality of bioassay organisms.

The principle objectives of this study were

- to establish the degree to which metals in the harbour sediment are biologically available,
- to compare the biological response of test organisms exposed to harbour sediment with weak acid extractions of metals from that sediment,
- to relate toxicity observed in bioassays to the oxygen regime in overlying water which varied depending upon sampling date, and
- to evaluate tissue residues of contaminants in test organisms in light of sediment contamination and extractable metal concentrations.

While PAH contamination is a serious consideration in zones within the harbour, this study was designed to examine locations where PAH concentrations were relatively low. A similar assessment on PAH bioavailability in Hamilton Harbour sediment is recommended to design a comprehensive strategy for sediment rehabilitation.

Materials and methods

Field sample collection

In phase one of the study, sediment was collected by a Shipek grab sampler in November 1989 and the surface two cm were removed from each grab using acid-washed and hexane rinsed plastic spoons. Approximately 20 litres of surficial sediment was placed in collection buckets lined with polyethylene bags, which were then sealed, kept cold in the field, and stored sealed and in the dark at 4 C for two to

then sealed, kept cold in the field, and stored sealed and in the dark at 4 C for two to four weeks prior to conducting the bioassays (ASTM 1990, Bedard et al. 1992). Oligochaetes (tubificid worms) were collected by sieving sediment collected by Shipek grabs through a 500 μm Nytex mesh bag. Material retained in the sieve bags was placed in trays fitted with Nytex screen bottoms placed over receiving basins containing site water. The trays were held under lighted conditions for 12 to 24 h. The negative phototactic response of tubificids resulted in organisms falling through the top tray into the collecting basin. Oligochaetes were separated from detrital residue using Pasteur pipettes. Organisms were then placed for 24 hours in acid washed PET plastic bottles containing clean sediment in order to clear gut contents of contaminated sediment. These specimens were separated once again from the substrate, rinsed with distilled water, and were wrapped in plastic and frozen for metal analyses. Previous analysis of the clean sediment showed that metals and trace organic compounds were below the provincial Lowest Effects Level, a level at which potential contaminants are is considered to have no effect on the majority of sediment-dwelling organisms.

In phase two, aliquots of sediment for bioassays were collected at the same time as sediment for phase 1, stored at 4 C for three months, prepared for bioassays and transferred to bioassay chambers with aeration for an additional three months prior to the introduction of bioassay organisms. In phase three, sediment was collected in May 1990 as above from the same locations. Sediment pH, Eh and temperature were

measured on board at time of collection.

Sediment bioassays

Laboratory-reared test organisms were three month-old mayfly nymphs (Hexagenia limbata) weighing approximately 4 mg.individual^{-1} (wet weight), 3 to 4 month old juvenile fathead minnows (Pimephales promelas) weighing approximately 300-400 mg.individual^{-1} wet weight and second-instar chironomid larvae (Chironomus tentans). Growth, mortality, and bioaccumulation of contaminants were the endpoints measured. The sediment bioassay protocol is detailed by Krantzberg (1990a) and Bedard et al. (1992). Two-litre wide mouth glass jars of surface area 100 cm^2 were filled to a depth of 3 cm with sieved, homogenized sediment and 1,200 ml of deionized water to obtain a water:sediment ratio of 4:1 (v/v). The sediment test chambers were allowed to settle overnight. Aeration was provided one hour prior to addition of the test organisms and continued throughout the duration of the experiment. Water loss due to evaporation was replaced as necessary to retain the appropriate volumetric ratio of water to sediment. Dissolved oxygen, pH, conductivity and temperature were monitored routinely during the experiments.

Starting biomass was measured on 30-50 randomly collected mayfly nymphs or fathead minnows. These individuals were not used in the sediment bioassays. Ten individual mayflies or fathead minnows were allocated to triplicate bioassay chambers

assembled for each station. Following 21 days, the beakers were harvested for surviving individuals. Fresh weights were measured on surviving individuals at the termination of the exposure. For chironomids, triplicate chambers of fifteen individuals were exposed for 10 days at a 16h:8h photoperiod, to permit development to the fourth instar and termination of the experiment prior to pupation. Individual fresh biomass was measured on surviving organisms. Experimental chambers were held in a water bath set at 22 C.

Surviving fathead minnows were placed into 30 ml glass vials and frozen for subsequent trace metal analyses. Honey Harbour sediment (Georgian Bay, Lake Huron), the sediment in which mayflies were reared for use in the bioassays, was used as a negative control sediment to monitor growth and mortality.

Oxygenation experiment

During phase two, bioassay chambers were prepared and held at 8 C in a temperature controlled water bath. Air lines were inserted below the water surface and a gentle stream of air was bubbled for three months time. Water lost through evaporation was continually replaced. Upon introduction of test organisms, bioassay design was identical to phase one and phase three.

Sediment characterization

Sediment chemistry was measured on whole sediment and the <63 μm size fraction. For both size classes, total metals were analyzed based on *aqua-regia* digestions.

Organic content was characterized by % loss on ignition, NH_3, NO_2, NO_3, TKN, total organic carbon, total phosphorus. In addition, particle size distribution was determined. Methods followed the protocol of Environment Ontario (OMOE 1983), with particle size estimated using the pipette method (Rukavina and Duncan, 1970).

For the <63 μm size class, separate aliquots were leached using one of two weak acid extractants. Sediment was thoroughly homogenized by stirring with a polyethylene spatula. Sediment was wet-sieved using a minimal amount of distilled water to retrieve the <63 μm size fraction. The exact volume of water and mass of sediment used was recorded and the elutriate analyzed for metals and nutrients. All subsequent testing and analyses were performed on the fine fraction. Representative samples (< 63 25 μm) were dried in order to permit future conversion of concentrations from fresh sediment to a dry weight expression.

For the chemical extractions, triplicate aliquots of each fine sediment were extracted by placing the equivalent of 0.5 gm dry weight of sediment in acid washed 50 ml polyethylene centrifuge tubes, to which were added the reagents described in the following procedures:

Hydrochloric Acid

continuous shaking of fresh sediment with 20 ml analytical grade 1.0 N HCl for 5 hours, followed by centrifugation at 15000 rpm for 15 min. The supernatant pH was measured to insure that acidity was sufficiently buffered. The residue was rinsed with distilled water, centrifuged, and

the supernatant rinse water discarded. The pellet was then digested using aqua regia.

Hydroxylamine-hydrochloride

continuous shaking of fresh sediment for 6 hours at 90 C with 20 ml analytical grade 0.1N hydroxylamine-hydrochloride, acidified to pH 2 with 25% glacial acetic acid . These were centrifuged and treated as above, including digestion using aqua regia.

Aqua Regia

Additional aliquots were digested using aqua regia without being previously extracted. These samples were used to confirm the recoveries observed in the (a) or (b) procedures.

Appropriate quality assurance included use of standards, reagent blanks, spikes and standard reference materials (Beak 1991). Spike recoveries varied from 75 to 104%. Metal recoveries from standard reference materials were within 10% of certified values and blank values ranged from undetectable to 0.03 mg/L.

Results

Field observations

Eh measurements of the sediment were all marginally positive, indicating that surface sediment was slightly oxic, however Eh values could be misleading as a consequence of sediment handling, in spite of efforts to minimize disturbance of the sediment (Table 1). Values for sediment collected in the spring tended to be higher than those from

sediment collected in the fall. The anoxic odour noted during collection suggests that the sediment would have had negative Eh values *in situ*. Station locations are illustrated in figure 1.

Sediment bioassays

Mayflies:

The most severe mortality was associated with sediment collected in the fall of 1989 (Fig. 2). For stations 20 and 258, mortality differed significantly with toxicity being greater in the fall (phase 1), followed by the oxygenated sediment (phase 2) and least in the spring (phase 3). For other stations, mortality was not an endpoint with sufficient sensitivity to differentiate sediment locations (Bedard and Petro, 1991)

Biomass changes were marginally influenced by date of collection and oxygenation (Fig. 2), with growth exceeding that of controls in stations 252, 260 and 270. Analysis of variance and Tukey's multiple range test revealed highly significant ($p<.001$) differences in responses among stations, with the growth endpoint distinguishing stations 252, 260 and 270 as different from controls and from stations 20 and 258 (Bedard and Petro, 1991).

Chironomids

In phase one, chironomid mortality was significantly greater than controls at stations

20, 258 and 260. Due to excessive control mortality during phases two and three, the effects of oxygen regime could not be evaluated (Fig. 3).

As with the mayflies, growth successfully discriminated among stations during phase one, with stations 252, 260 and 270 eliciting significantly greater growth (ANOVA, $p<.001$) than stations 20 and 258. Growth in stations 20 and 258 sediment collected in the spring was significantly greater than growth observed from fall sediment collections. Mortality at these stations in the fall collection (Fig. 3) was approximately 20%, although the spring data for mortality should be regarded with caution.

Fathead minnows

No mortality occurred for fathead minnows exposed to Hamilton Harbour sediment under any of the oxygenation scenarios.

Tissue residues of contaminants in laboratory and field organisms

Metal concentrations in fathead minnows varied with sediment type and with the nature of the oxygen regime (Table 2). With the exception of Ni and Mn at station 258, metal concentrations in minnows were significantly ($p<0.001$) greater in fall (phase one) test organisms than in spring (phase three) samples. The highest concentrations of Ni and Cr in oligochaetes were from organisms collected from stations 258 and 260, with highest concentrations of Pb, Cd, Cu, and Hg, occurring in station 260 ($p < 0.05$).

Chemical analyses

Metal concentrations in weak acid extracts from spring and fall sediment are presented in Figures 4 - 14 along with metal concentrations in fathead minnows. Since metals were analyzed on aliquots of homogenized sediment, values are assumed to be comparable to the aliquots used in actual laboratory exposures. Metals in fish were significantly correlated with metals extracted by $NH_2OH.HCl$ with the exception of Al. In contrast, only three of the 10 metals measured (As, Cu and Mn) were significantly correlated with metals extracted from whole sediment using aqua regia (Table 3), and this declined to two (Cu and Ni) when the acid digestion involved the < 63 μm size fraction. Five of the metals extracted in 1N HCl (As, Cd, Fe, Mn, and Zn) were significantly correlated with metals in bioassay minnows. In those stations where metals in fathead minnows were greater following exposure to fall sediment as compared to spring sediment, metals concentrations in the $NH_2OH.HCl$ extract followed the same pattern, while metals concentrations in bulk sediment did not. R^2 values for simple regressions demonstrate that an equal or greater amount of variability in fathead minnow tissue concentrations is explained by metal concentrations in the $NH_2OH.HCl$ extract as compared with bulk sediment chemistry (Table 4).

Nutrient content and particle size varied among sites, but was consistent between sampling periods (Table 1). No clear relationship between sediment toxicity and substrate characteristics was apparent over all, however, in phase 1 mayfly mortality

and chironomid growth were significantly correlated with total organic carbon and particle size.

Discussion

In the fall bioassays, growth by both mayfly nymphs and chironomid larvae distinguished stations 20 and 258 as more toxic than stations 252, 260 and 270. Mayfly mortality also identified stations 20 and 258 as the most toxic. Metal concentrations of As, Cd, Cr, Cu, Pb and Zn in fathead minnows were highest following exposure to sediment from station 258, leading to a marked degree of concurrence among a variety of bioassay organisms and endpoints.

For the more toxic stations, mayfly survival (stations 258 and 20) and growth (station 258) was poorer in the fall as compared to the spring. For example, mayfly mortality when exposed to sediment from station 20 declined from 23% in the fall to 0 % in the spring. The respective values for station 258 were 17% and 3%. Fathead minnow tissue residues of Zn, As, Hg and Cd were significantly greater in the fall exposures, with Cu, Cr and Pb following a similar pattern for most stations, and consistently so for stations 20 and 258. The pattern of higher $NH_2OH.HCl$ extractable metals in sediment and higher tissue residues in fathead minnows in fall as compared to spring sediment bioassays suggests that metal bioavailability is greater following conditions of summer anoxia (fall) than when bottom waters have been oxic since fall overturn (spring). In turn, if metal bioavailability is greater, the potential for sediment to elicit lethal and

sublethal effects as mirrored by the mayflies, is enhanced at some locations.

If metal coprecipitation by Fe and Mn hydroxides is important in regulating metal speciation in Hamilton Harbour, then the dissolution of hydroxides under reducing conditions could result in greater trace metal bioavailability. There is good evidence that benthic species accumulate contaminants through ingestion (Nalepa and Landrum 1988, Timmermans et al 1992, Hare et al 1991, Luoma et al 1992, Krantzberg 1990b). Percolation of Fe and Mn through anoxic pore water could result in the coprecipitation of metals with newly formed Fe/Mn oxides at the sediment surface. Metals extracted with low molarity hydroxylamine-hydrochloride solutions have been operationally defined as easily reducible, in the form of amorphous Fe and Mn hydroxides (Campbell and Tessier 1989, Forstner 1987), and it was this metal phase that was most strongly correlated with fathead minnow tissue residues. Luoma (1989) has established a positive correlation between the Fe/Mn content of sediment and concentrations of various trace metals in benthos exposed to those sediments. Forstner (1987) also found that weak acid-reducing extractions yielded an estimate of the mobile and potentially available fractions of certain metals.

The formation of insoluble coprecipitates following the incursion of oxygenated water during fall overturn and the subsequent aging of those coprecipitates could reduce metal bioavailability (Forstner and Wittman 1981), as suggested by decreased sediment toxicity, decreased metal extractability, and decreased bioaccumulation.

It is plausible, then, that there is a link between the greater tissue burdens in fathead minnows and the toxicity observed in other test species. Although accumulation of metals in test organisms and toxicity were reduced less during spring as compared to fall exposures, contaminants could continue to limit benthos *in situ*, even if hypolimnetic oxygen depletion was rectified. This is apparent when comparing tissue residues in bioassay organisms with those exposed to reference sediment. Nevertheless, oxic conditions did apparently result in reduced bioaccumulation and toxicity.

Stations 20 and 258 were the most toxic to benthic organisms, however, this was not mirrored by tissue residues in oligochaetes collected from those stations (Fig. 4 - 14). It is evident that bioaccumulation of metals in laboratory organisms differs from that of field biota, a finding that may be attributed to interspecific differences in metal bioaccumulation. Lead, Cu, Cd, Fe and Mn concentrations in tubificids exceeded those in fathead minnows with few exceptions, which concurs with literature findings that these metals do not biomagnify (Burrow and Whitton 1983, Dallinger and Kautzky 1985, Timmermans et al. 1989).

Alternatively, differences between oligochaete tissue concentrations and those in fathead minnows could be a result of changes in metal speciation during sediment manipulation for bioassays. The anoxic nature of Hamilton Harbour sediment may result in the formation of sulfide metal complexes that would limit metal

bioaccumulation. DiToro et al (1989) have proposed that solid-phase acid-volatile sulfide can bind metals such as Cd and Ni in sediment, thereby limiting their bioavailability and the toxicity of contaminated sediment. Dissolution of those complexes upon bioassay assembly and sediment preparation for metal extraction could transform the metal species into more bioavailable forms.

Luoma and Carter (1991) point out the need for examining temporal variability in metal exposures of biota, citing seasonal redistribution of fine-grained, metal-enriched sediment as important in year-to year changes in contaminant exposures in San Francisco Bay. In the case of Hamilton Harbour, an additional influence of seasonal changes in contaminant exposure could be a result of changing physicochemical conditions that alter metal speciation and toxicity. Temporal variation in metal exposure *in situ* may have contributed to the divergence between oligochaete and fathead minnow tissue concentrations. The exposure duration for resident benthos is clearly greater than the 21 day exposure for fathead minnows, and this could effect metal retention and tissue concentrations.

Conclusions

Sediment in areas of the harbour, such as those at stations 260 and 270, have concentrations of metals that are above the provincial Severe Effect Level, but were not lethal to test organisms, while at other locations such as stations 20 and 258,

toxicity was significantly different from controls. Based on evidence from weak acid extraction of metals from sediment, the differences among stations is likely due to differences in the bioavailability of contaminants. More sensitive measurements of the bioavailable portion of metals in sediment are needed, and extraction of metals from sediment using hydroxylamine-hydrochloride holds promise for estimating the bioavailable portion of metals in sediment.

The data indicate that sediment toxicity was greater when samples were collected in the fall as compared to the spring. Anoxia is known to develop periodically in the hypolimnion, during the summer months in Hamilton Harbour. While seasonal variation in toxicity may be attributed to sediment oxygen demand, metal bioavailability as measured by hydroxylamine-hydrochloride extractions and bioaccumulation by fathead minnows, was greater in the fall than in the spring. While the macroinvertebrate community is clearly restricted as a consequence of summer anoxia, metal contamination in some areas of the harbour is a substantive issue. While the elimination of periods of oxygen depletion in the harbour's hypolimnion will assist in reducing sediment toxicity, the elevated tissue residues in fathead minnows and mortality and growth impairment in chironomid larvae and mayfly nymphs support the need for additional sediment remediation.

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TABLE 1. REDOX POTENTIAL, NUTRIENT CONTENT AND PARTICAL SIZE OF SEDIMENT FROM HAMILTON HARBOUR. ALL VALUES IN μg/g DRY WEIGHT UNLESS OTHERWISE NOTED. STATION NUMBERS FOLLOWED BY THE DIGITS 1 AND 3 WERE COLLECTED IN FALL AND SPRING, RESPECTIVELY. (Eh = redox potential, LOI = loss on ignition, TOC = total organic carbon)

STATION	Eh (mV)	NH_3	NO_2	NO_3	TKN	%TOC	TOTAL P	%LOI	% SAND	%SILT	%CLAY
HAMILTON HARBOUR CONTROL	103	4.4	0.03	.063	3100	2.68	950	6.1	57.0	39.5	3.5
HONEY HARBOUR CONTROL	289	1.2	0.37	2.7	2500	5.67	3300	6.6	63.9	27.6	8.5
20-1	20	32	0.10	0.64	4000	5.28	3300	16.8	34.9	57.1	7.9
20-3	102	34	0.10	0.50	4000	5.32	3200	16.4	32.9	58.6	8.5
252-1	65	6.3	0.05	2.8	1020	0.81	2000	6.1	85.2	12.5	2.1
252-3	80	6.6	0.05	2.9	980	0.71	1990	10.9	85.4	12.4	2.2
258-1	11	40	0.10	0.5	3400	6.02	4200	13.2	45.4	35.9	18.7
258-3	97	37	0.09	0.6	5200	6.3	4100	14.8	45.2	36.2	18.6
260-1	113	23	0.09	0.69	4500	4.46	5300	8.2	48.2	42.2	9.6
260-3	95	26	0.1	0.64	4700	4.18	5200	9.2	47.8	39.1	11.2
270-1	84	38	0.16	0.85	4800	4.36	2700	16.6	51.1	36.39	12.5
270-3	109	40	0.18	0.8	4900	4.44	2700	16.6	51.6	36.9	11.5

Table 2: **METAL CONCENTRATIONS IN FATHEAD MINNOWS EXPOSED TO HAMILTON HARBOUR SEDIMENT IN THE FALL (PHASE 1) OF 1990 AND THE SPRING (PHASE 3) OF 1991. MEAN VALUES ARE IN UG.G^{-1} DRY WEIGHT ±S.D. AN ASTERIX DENOTES THAT THE FALL CONCENTRATIONS WERE SIGNIFICANTLY GREATER (P < 0.01) THAN THE SPRING CONCENTRATIONS.**

STATION	Al	Fe	Mn	Zn	As	Ni	Cr	Cu	Pb	Hg	Cd
Control-1	791	1317	47.3	230.5	0.88	7.37	2.72	4.62	1.3	0.848	0.36*
	±263	±437	±14.4	±24.9	±0.12	±0.77	±0.81	±0.41	±0.7	±0.169	±0.06
Control-3	535	967	44.6	179.0	0.70	6.18	2.18	3.79	0.9	0.806	0.15
	±60	±95	±7.6	±24.4	±0.08	±0.68	±0.31	±0.38	±0.5	±0.034	±0.03
270-1	1085	2968	173.8	333.0	2.22	11.75	11.40	9.86	15.1	0.626	0.36
	±125	±619	±61.7	±31.5	±0.29	±1.10	±1.79	±1.14	±2.8	±0.076	±0.06
270-3	893	2561	133.5	314.7	1.82	10.90	9.71	9.32	9.3	0.627	0.28
	±96	±450	±41.7	±22.1	±0.34	±1.18	±1.60	±2.93	±4.8	±0.109	±0.09
260-1	829	2686	132.9	378.8	2.35	11.51	12.22	9.13	11.9	0.748	0.35
	±162	±517	±32.7	±48.0	±0.36	±0.90	±2.64	±2.03	±6.7	±0.100	±0.12
260-3	960	3422	139.4	366.8	2.33	13.32	16.31	9.70	19.5	0.727	0.46
	±345	±1255	±64.6	±93.4	±0.56	±2.30	±5.71	±3.13	±6.5	±0.065	±0.15
258-1	1056*	3628 *	160.8	402.0*	2.40*	10.72	16.08*	10.96*	20.0*	0.733*	0.43*
	±59	±352	±20.6	±13.5	±0.18	±0.63	±1.35	±0.84	±1.9	±0.024	±0.04
258-3	737	2639	136.4	264.6	1.76	·10.10	10.80	7.28	13.6	0.269	0.25
	±39	±283	±19.4	±19.4	±0.19	±0.28	±1.00	±0.55	±1.1	±0.076	±0.02
20-1	622*	2575*	81.5	320.0*	1.39	8.69	13.55*	10.28	10.5*	0.762	0.27*
	±54	±680	±22.7	±9.3	±0.20	±2.79	±3.61	±1.99	±6.1	0.068	0.10
20-3	460	1497	58.4	251.5	1.14	8.19	6.05	6.92	5.7	0.640	0.11
	±22	±97	±5.0	±17.1	±0.05	±0.31	±0.31	±0.60	±0.3	±0.080	±0.01

TABLE 3. CORRELATION BETWEEN METALS IN VARIOUS HAMILTON HARBOUR SEDIMENT EXTRACTS WITH METALS IN BULK SEDIMENT (WHOLE SEDIMENT DIGESTED IN AQUA REGIA) AND METALS IN FISH (BIOASSAY FATHEAD MINNOWS). VALUES UNDERLINED ARE SIGNIFICANT AT P<0.05.

PARAMETER	NH2OH.HCl	HCl	BULK<2mm	BULK<63 μm
Al, BULK<2mm	-0.15	0.08		0.74
Al, FISH	0.54	-0.19	-0.09	0.17
As, BULK<2mm	0.28	0.83		0.42
As, FISH	0.67	0.59	0.84	0.58
Cd, BULK<2mm	0.09	0.07		0.96
Cd, FISH	0.67	0.67	-0.02	0.03
CR, BULK<2mm	0.28	0.15		0.78
Cr, FISH	0.67	0.40	0.40	0.55
Cu, BULK<2mm	0.50	0.06		0.92
Cu, FISH	0.67	0.02	0.63	0.62
Fe, BULK<2mm	0.24	0.24		0.45
Fe, FISH	0.62	0.79	0.50	0.18
Mn, BULK<2mm	0.35	0.40		0.16
Mn, FISH	0.75	0.79	0.58	0.41
Ni, BULK<2mm	0.65	0.71		0.69
Ni, FISH	0.76	0.38	0.56	0.83
Pb, BULK<2mm	0.23	0.29		0.64
Pb, FISH	0.71	0.51	0.51	0.55
Zn, BULK<2mm	0.46	0.47		0.73
Zn, FISH	0.94	0.95	0.52	0.39

TABLE 4. R-SQUARE VALUES FOR LINEAR REGRESSIONS BETWEEN METALS IN FATHEAD MINNOWS AND METALS IN HAMILTON HARBOUR SEDIMENT EXTRACTED WITH DIFFERENT REAGENTS.

METAL	NH2OH.HCL	HCL	BULK (<2 mm)	BULK (< 63 μm)
ALUMINUM	29.3	3.6	0.9	3.2
CADMIUM	44.2	44.7	0.1	0.0
COPPER	44.7	0.1	40.7	38.6
IRON	38.5	61.6	25.0	3.0
MANGANESE	56.2	62.1	34.0	16.8
NICKEL	57.2	14.2	31.4	69.3
LEAD	50.1	25.9	26.8	31.2
ZINC	87.9	90.5	28.1	15.1

FIGURE 1. STATION LOCATIONS FOR SEDIMENT COLLECTIONS, HAMILTON HARBOUR, LAKE ONTARIO.

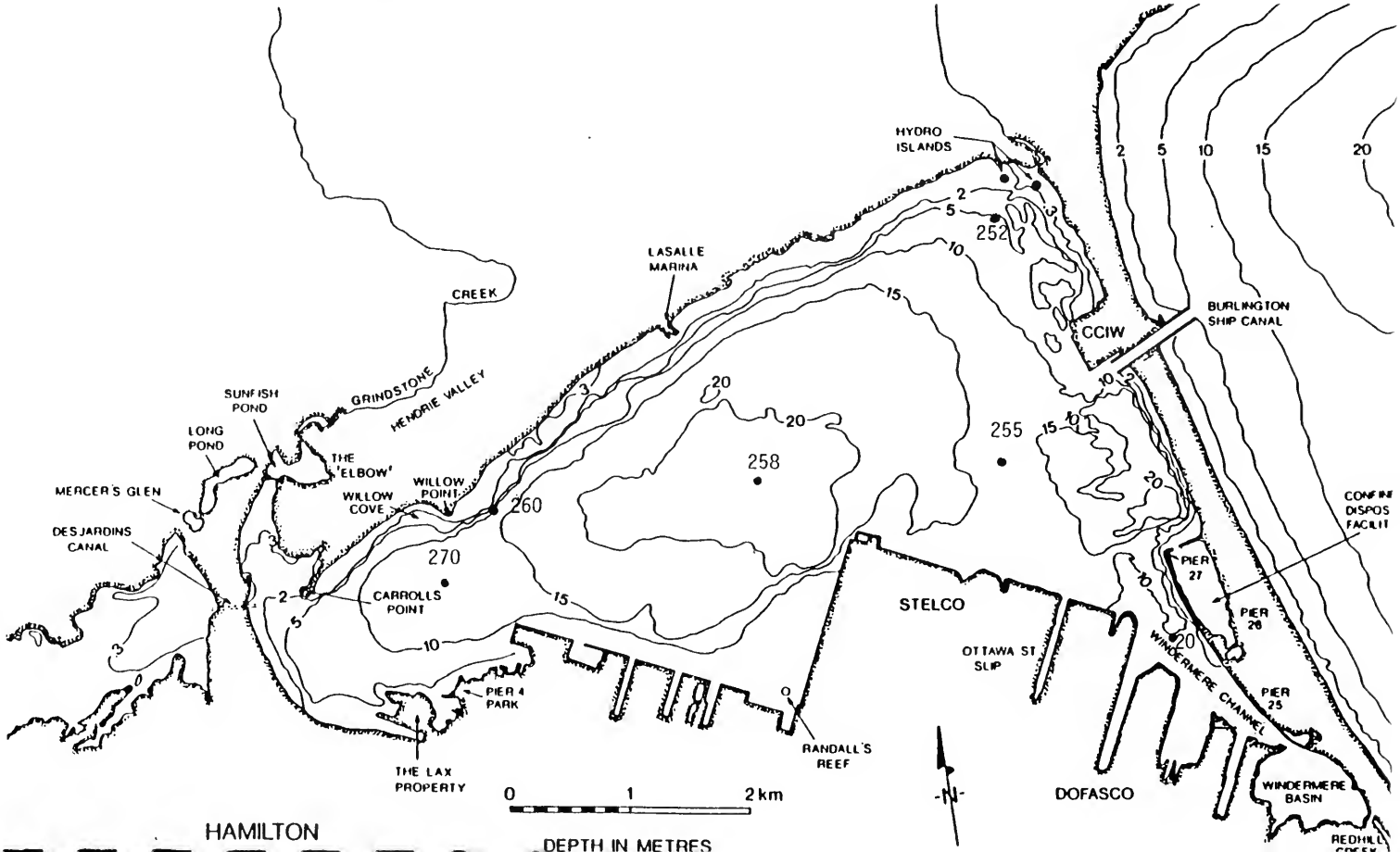
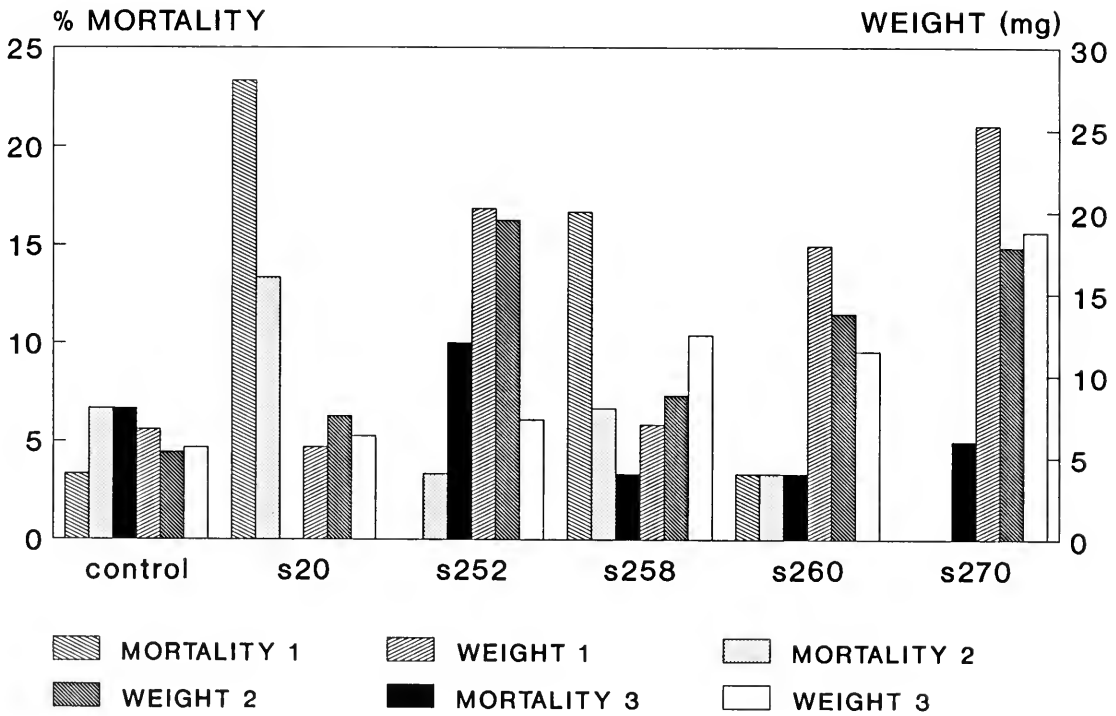


FIGURE 2

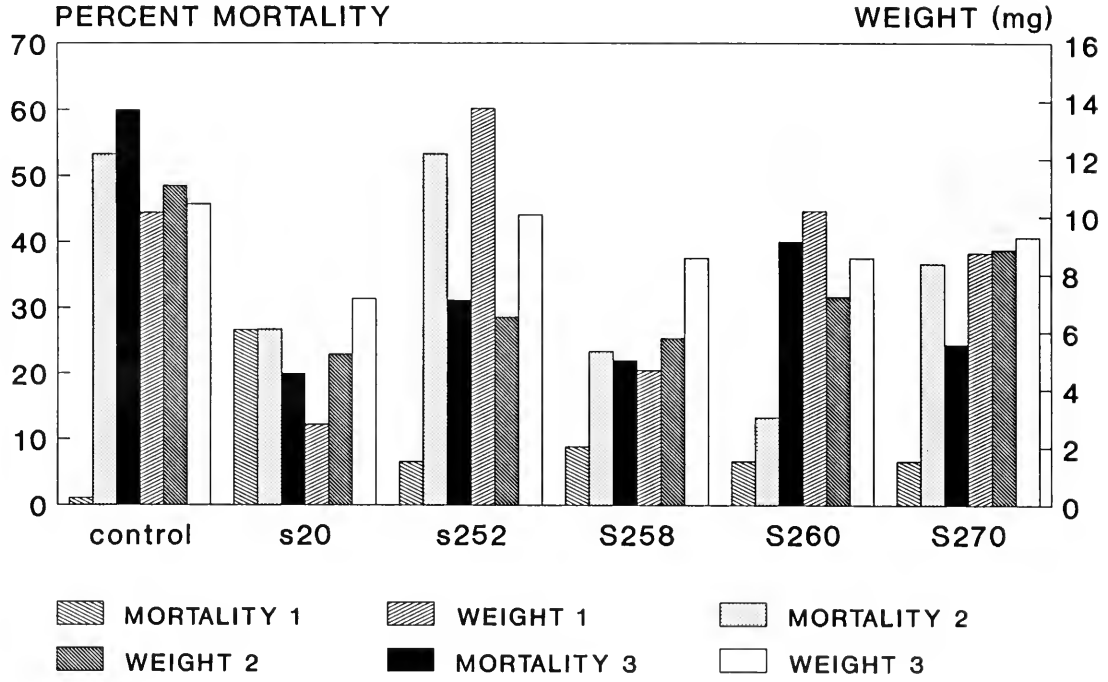
MAYFLY BIOASSAY, HAMILTON HARBOUR 89/90
OXYGENATION EFFECTS *



*1, 2, and 3 represent the first, second and third phases

FIGURE 3

CHIRONOMID BIOASSAY, HAMILTON 1989/90
OXYGENATION EFFECTS *

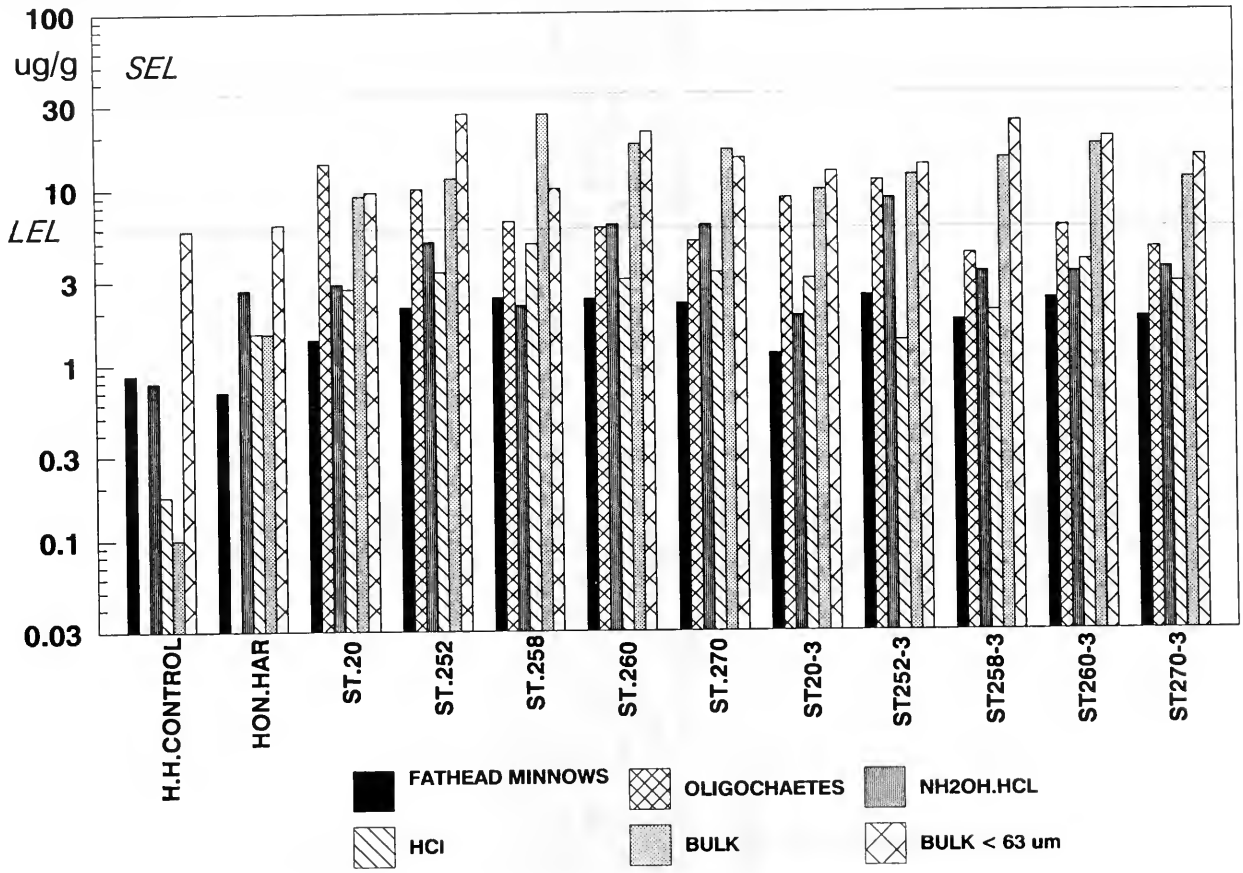


*1, 2, and 3 denote the first, second and third phases

FIGURES 4 - 14:

METAL CONCENTRATIONS IN FATHEAD MINNOWS USED IN HAMILTON HARBOUR SEDIMENT BIOASSAYS, NATIVE OLIGOCHAETES, AND SEDIMENT EXTRACTS FROM BULK AND SIEVED (< 63 μm) SEDIMENT. ALL VALUES ARE IN μg/g DRY WEIGHT AND REPRESENT THE MEAN OF FIVE (BIOTA) AND THREE (SEDIMENT) REPLICATES (coefficient of variation < 10%).

Arsenic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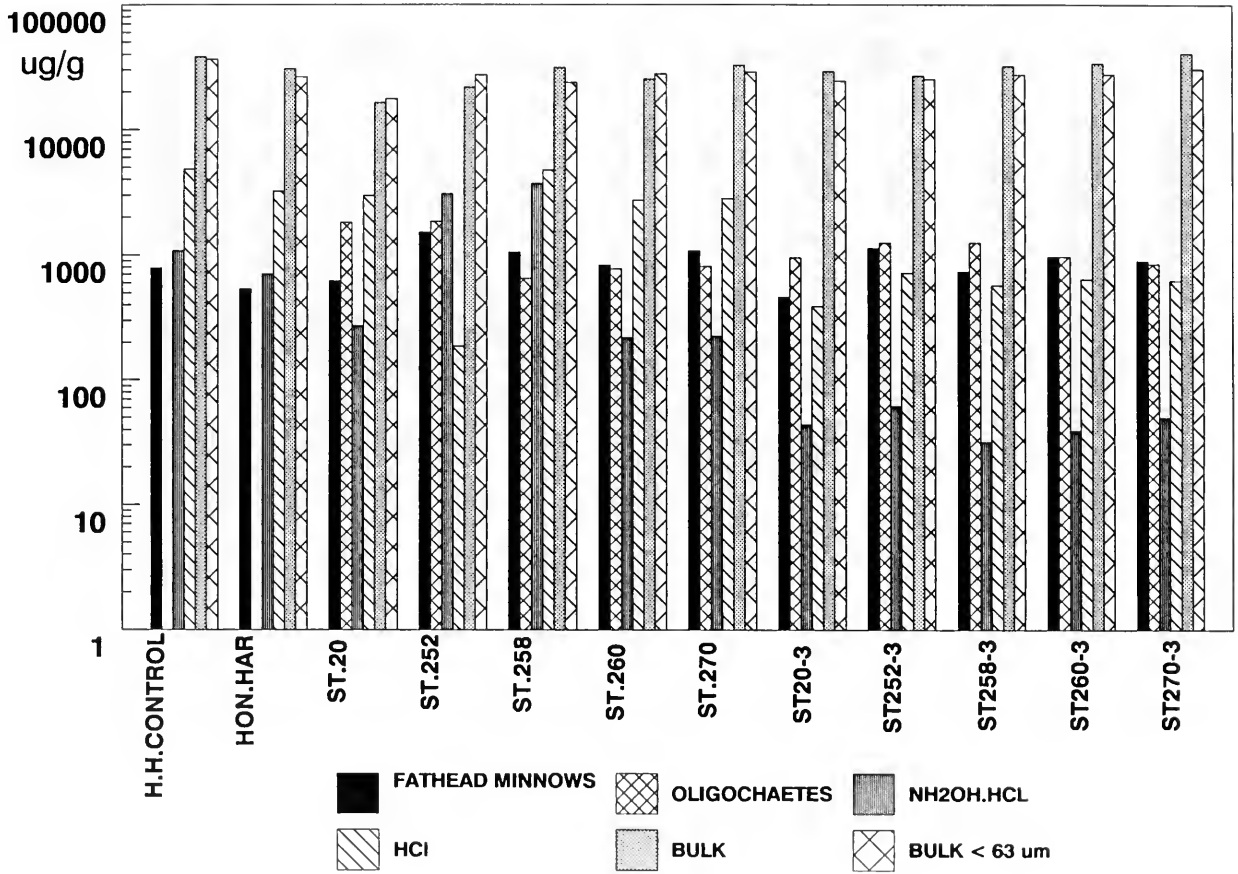
ug/g
SEL
30
10
LEL
3
1
0.3
0.1
0.03
H.H.CONTROL
HON.HAR
ST.20
ST.252
ST.258
ST.260
ST.270
ST20-3
ST252-3
ST258-3
ST260-3
ST270-3
FATHEAD MINNOWS
OLIGOCHAETES
NH2OH.HCL
HCl
BULK
BULK < 63 um

Aluminum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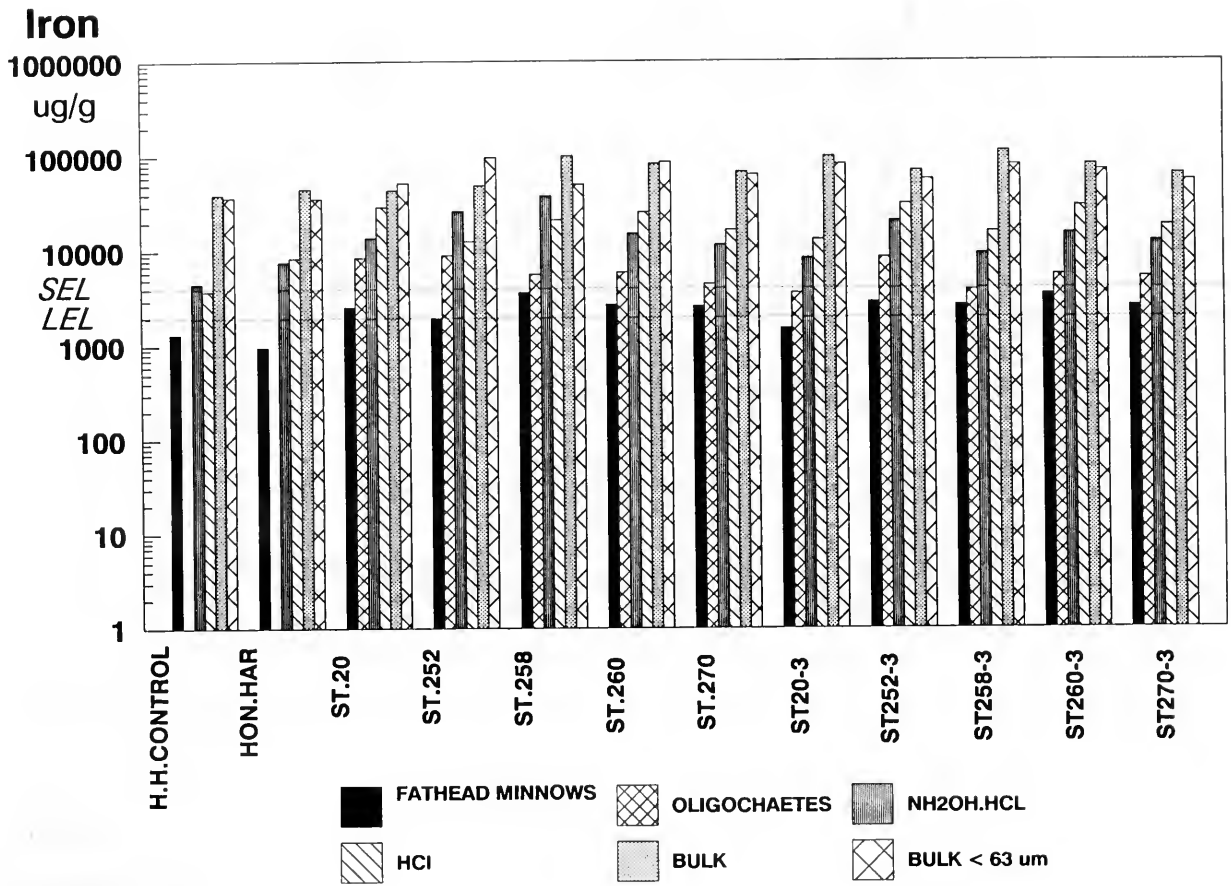
ug/g
10000
1000
100
10
1
H.H.CONTROL
HON.HAR
ST.20
ST.252
ST.258
ST.260
ST.270
ST20-3
ST252-3
ST258-3
ST260-3
ST270-3
FATHEAD MINNOWS
OLIGOCHAETES
NH2OH.HCL
HCl
BULK
BULK < 63 um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ug/g
100000
10000
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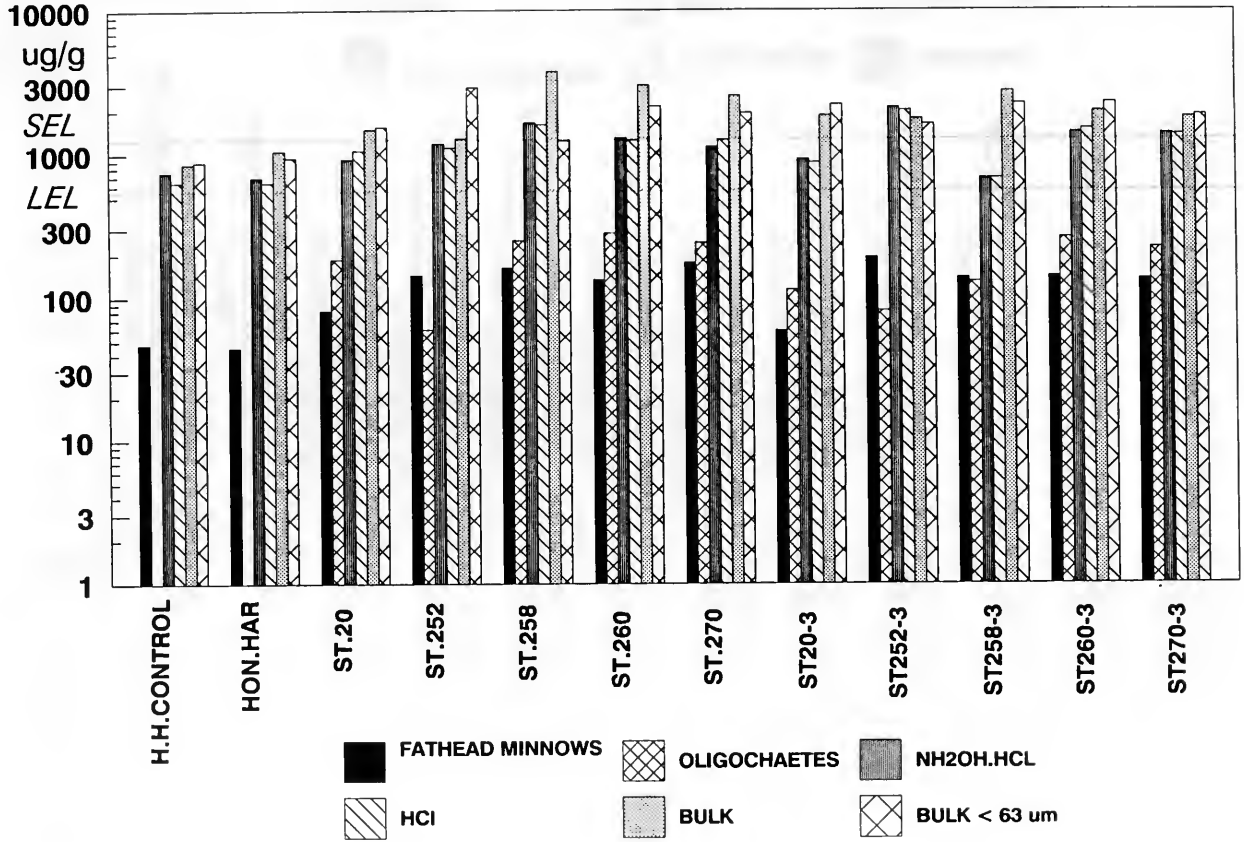
LEL
1000
100
10
1
H.H.CONTROL
HON.HAR
ST.20
ST.252
ST.258
ST.260
ST.270
ST20-3
ST252-3
ST258-3
ST260-3
ST270-3
FATHEAD MINNOWS
OLIGOCHAETES
NH2OH.HCL
HCl
BULK
BULK < 63 um

Manganese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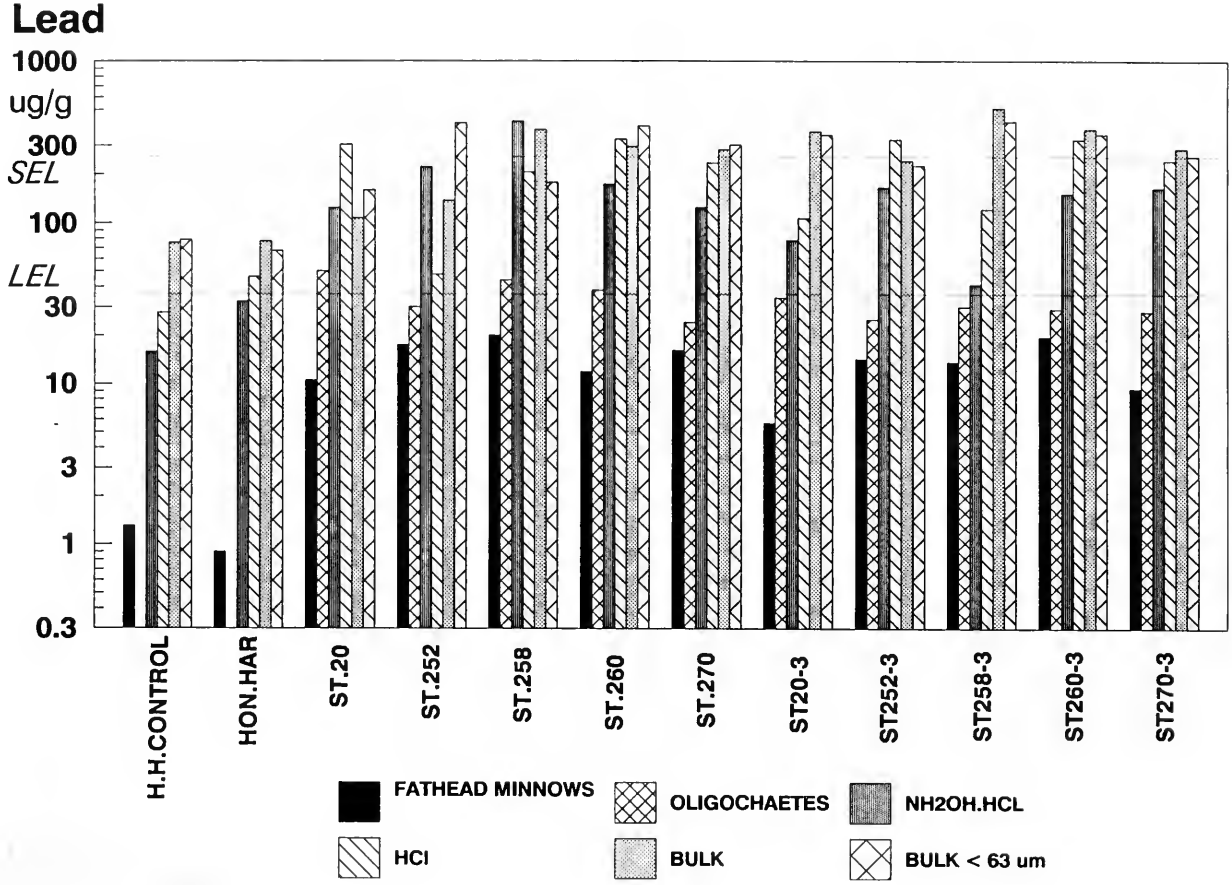
ug/g
3000
SEL
1000
LEL
300
100
30
10
3
1
H.H.CONTROL
HON.HAR
ST.20
ST.252
ST.258
ST.260
ST.270
ST20-3
ST252-3
ST258-3
ST260-3
ST270-3
FATHEAD MINNOWS
OLIGOCHAETES
NH2OH.HCL
HCl
BULK
BULK < 63 um


Lead
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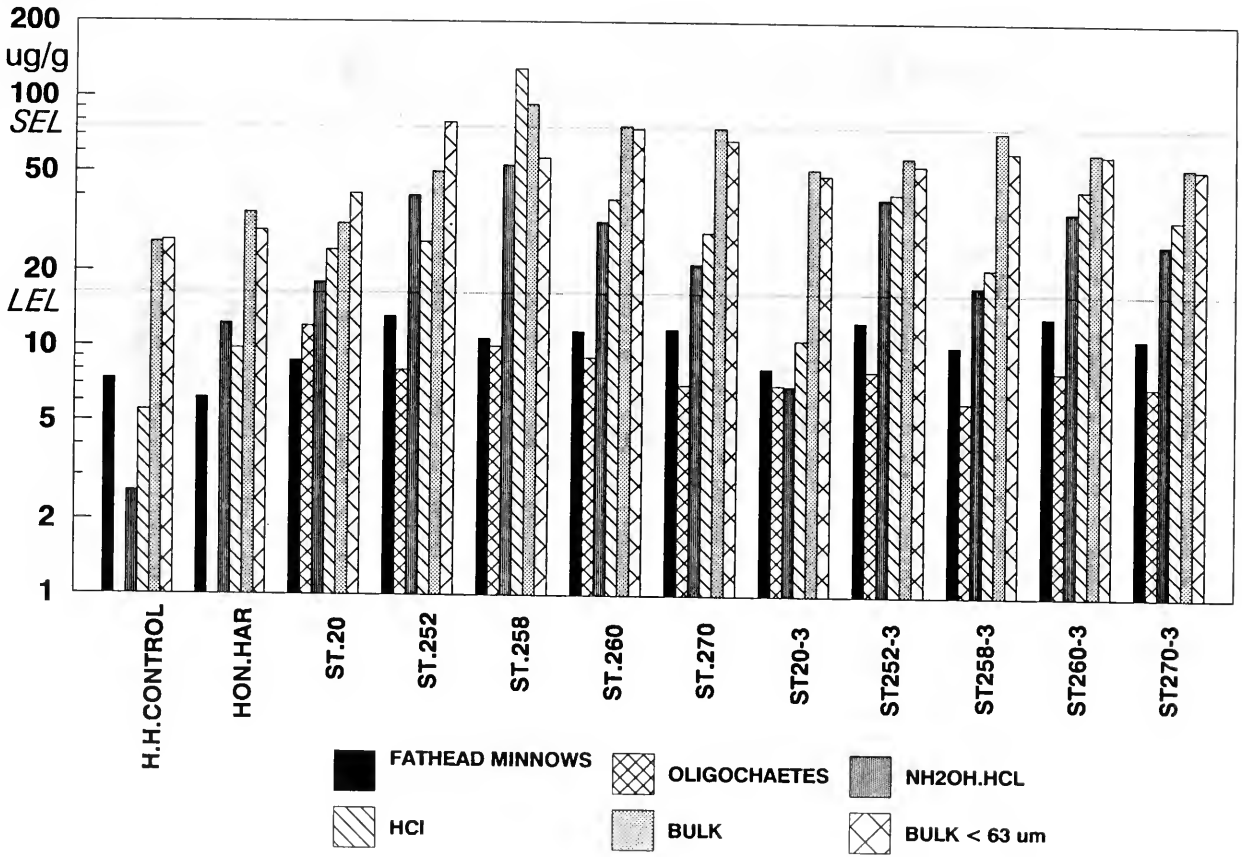
ug/g
300
SEL
100
LEL
30
10
3
1
0.3
H.H.CONTROL
HON.HAR
ST.20
ST.252
ST.258
ST.260
ST.270
ST20-3
ST252-3
ST258-3
ST260-3
ST270-3
FATHEAD MINNOWS
OLIGOCHAETES
NH2OH.HCL
HCl
BULK
BULK < 63 um

Nickel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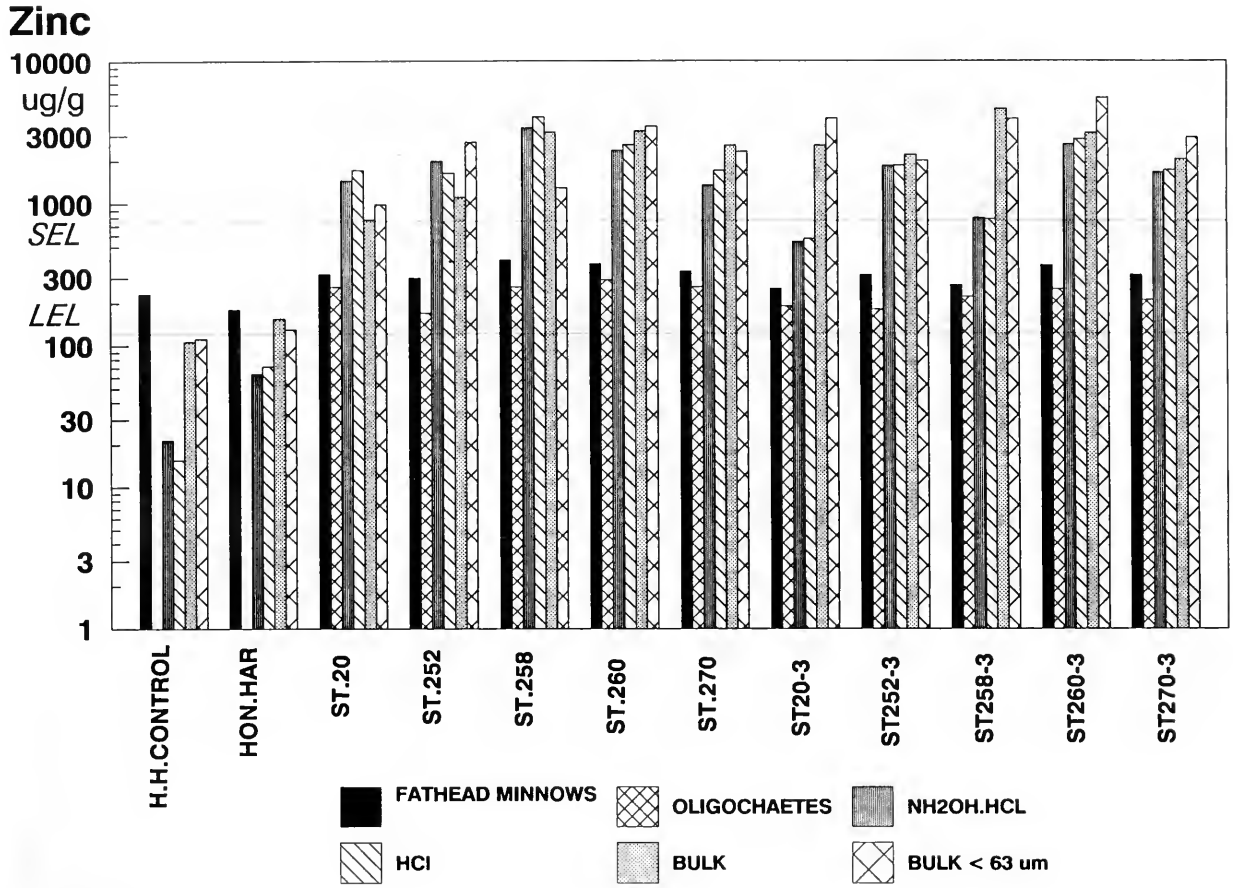
ug/g
100
SEL
50
20
LEL
10
5
2
1
H.H.CONTROL
HON.HAR
ST.20
ST.252
ST.258
ST.260
ST.270
ST20-3
ST252-3
ST258-3
ST260-3
ST270-3
FATHEAD MINNOWS
OLIGOCHAETES
NH2OH.HCL
HCl
BULK
BULK < 63 um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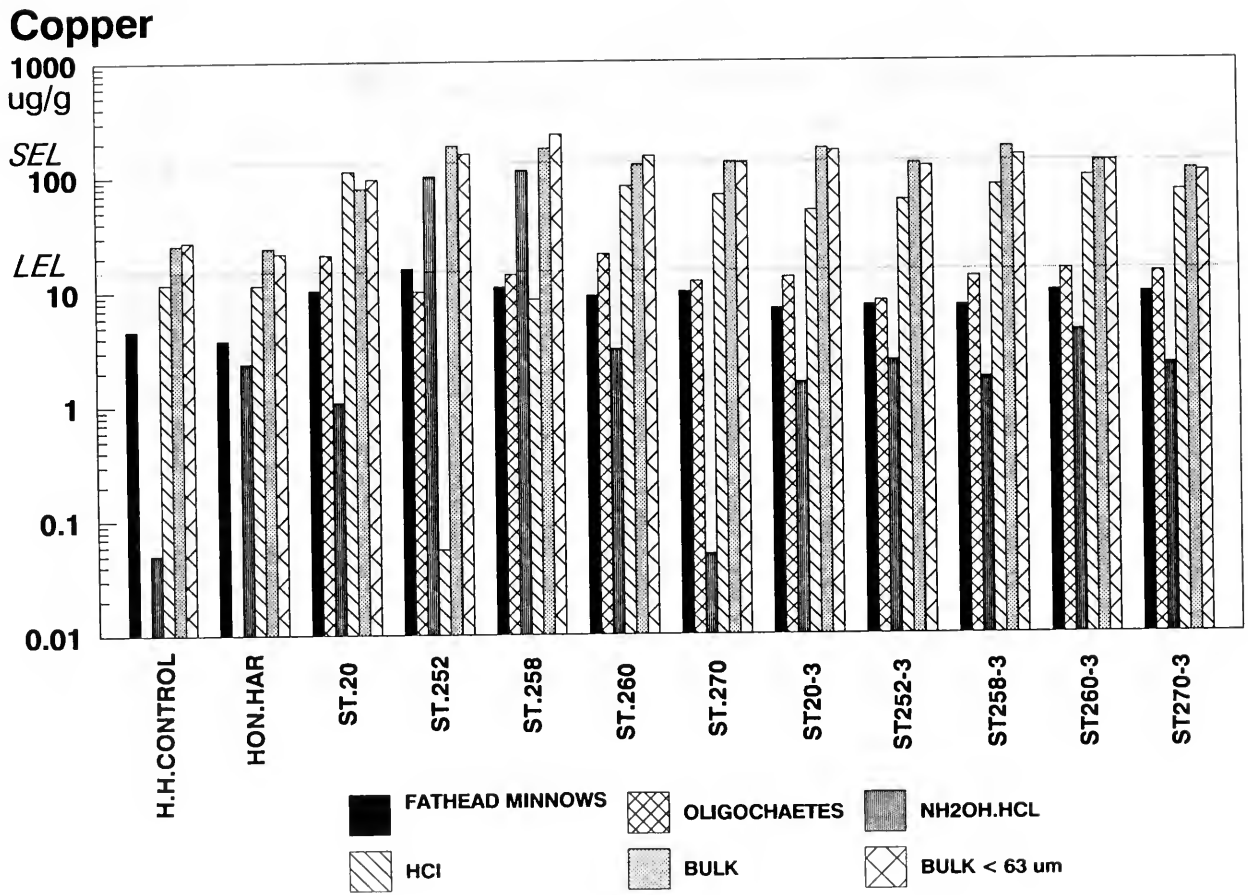
ug/g
3000
1000
SEL
300
LEL
100
30
10
3
1
H.H.CONTROL
HON.HAR
ST.20
ST.252
ST.258
ST.260
ST.270
ST20-3
ST252-3
ST258-3
ST260-3
ST270-3
FATHEAD MINNOWS
OLIGOCHAETES
NH2OH.HCL
HCl
BULK
BULK < 63 um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ug/g
SEL
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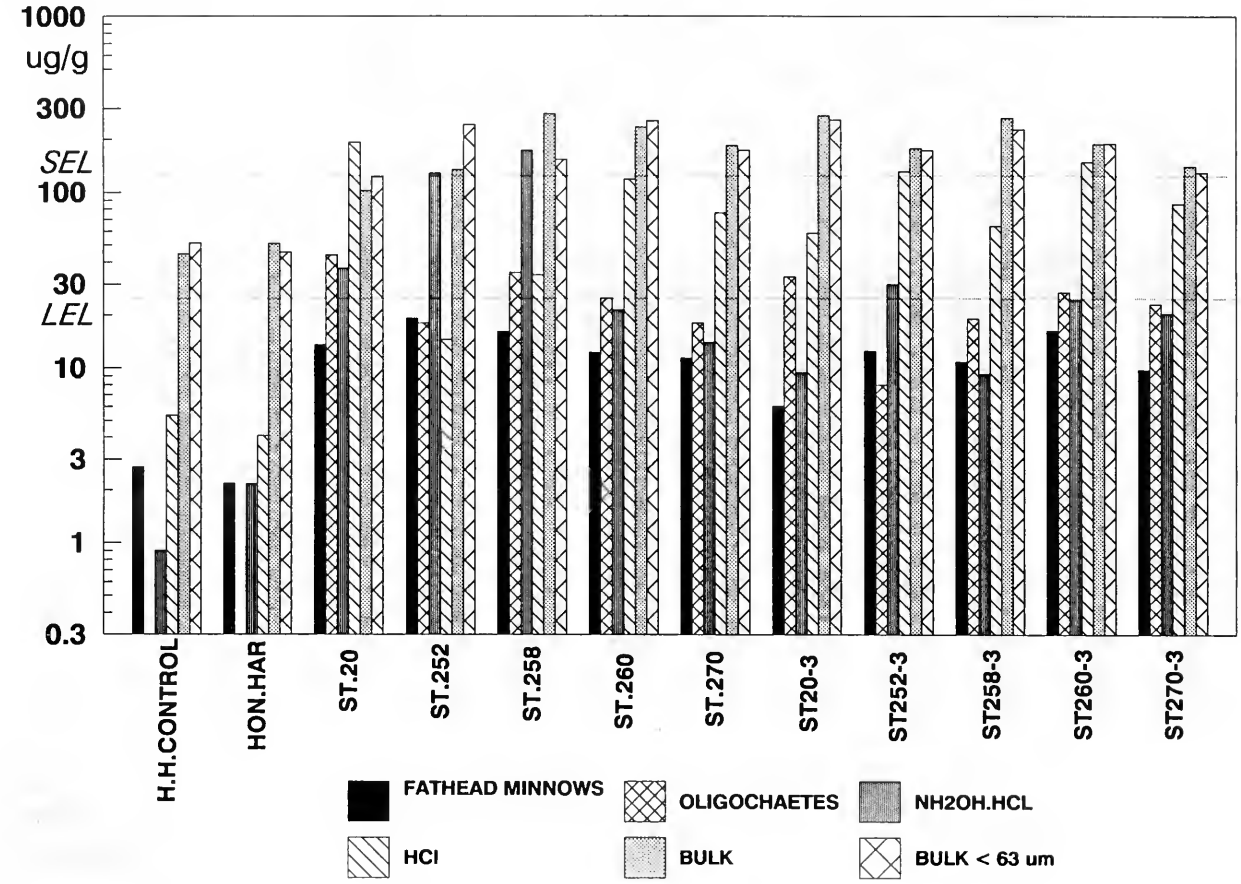
LEL
10
1
0.1
0.01
H.H.CONTROL
HON.HAR
ST.20
ST.252
ST.258
ST.260
ST.270
ST20-3
ST252-3
ST258-3
ST260-3
ST270-3
FATHEAD MINNOWS
OLIGOCHAETES
NH2OH.HCL
HCl
BULK
BULK < 63 um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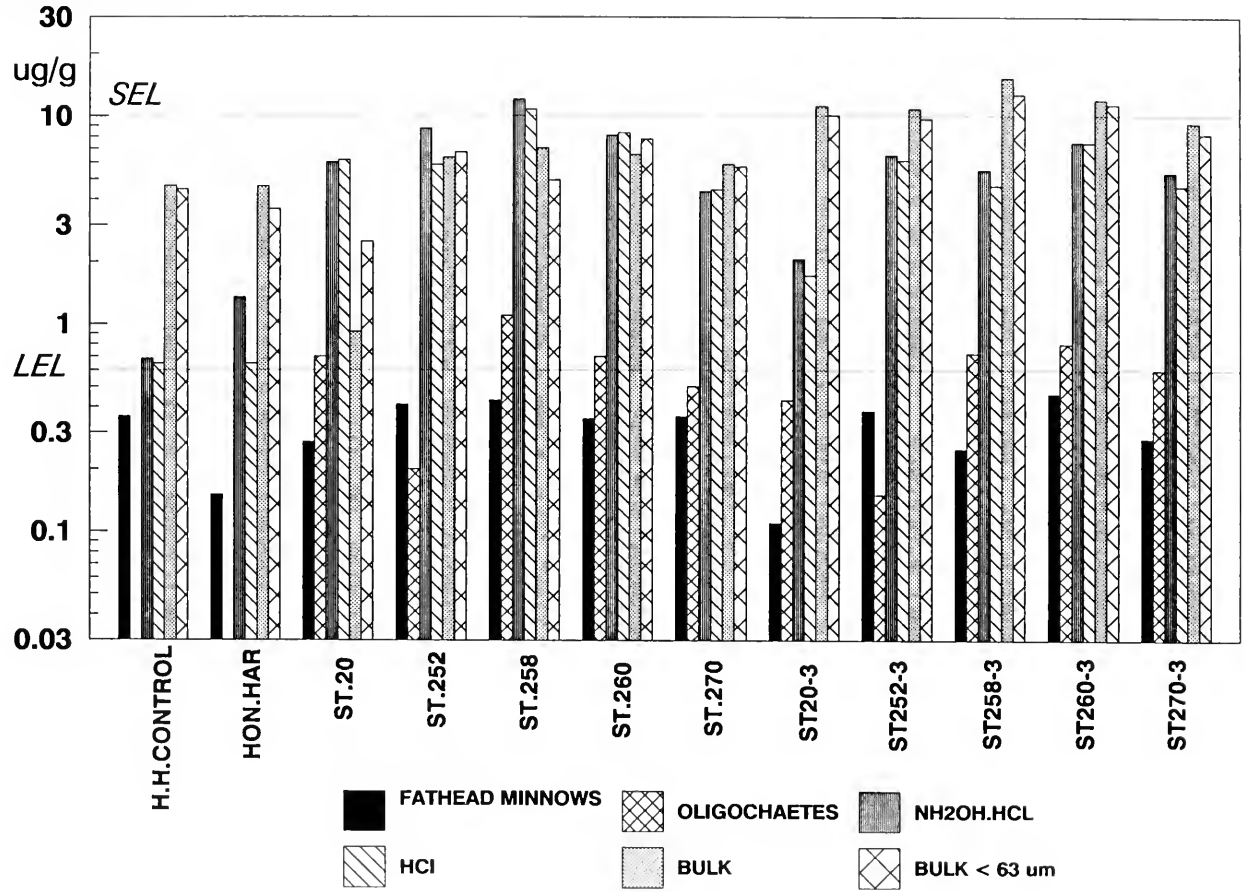
ug/g
300
SEL
100
30
LEL
10
3
1
0.3
H.H.CONTROL
HON.HAR
ST.20
ST.252
ST.258
ST.260
ST.270
ST20-3
ST252-3
ST258-3
ST260-3
ST270-3
FATHEAD MINNOWS
OLIGOCHAETES
NH2OH.HCL
HCl
BULK
BULK < 63 um

Cadmium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ug/g
SEL
10
3
1
LEL
0.3
0.1
0.03
H.H.CONTROL
HON.HAR
ST.20
ST.252
ST.258
ST.260
ST.270
ST20-3
ST252-3
ST258-3
ST260-3
ST270-3
FATHEAD MINNOWS
OLIGOCHAETES
NH2OH.HCL
HCl
BULK
BULK < 63 um